

PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Delustering of Shaped Polyamide Structures

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, located at Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synthetic linear polyamide shaped structures and more particularly to delustered polyamide yarns having improved light-durability.

Unpigmented yarns made from synthetic linear polyamides are somewhat more light-durable than the earlier man-made fibers, such as viscose rayon and cellulose acetate, considerably more light-durable than the continuous natural fiber, silk, and more nearly like the natural fibers linen and cotton in this respect. However, the addition of even minor amounts of many desirable titanium dioxide pigments as a delustering agent may appreciably reduce the light durability of the synthetic linear polyamide yarns. Furthermore, the addition of titanium dioxide delusterant in larger amounts up to 5% or 10% to obtain yarns having particular properties desirable for certain end uses, results in synthetic linear polyamides which degrade quite rapidly under certain conditions of light exposure.

Many end-uses for textile fibers require good light durability as well as the appearance and property characteristics which are achieved only through the addition of appreciable quantities of a delusterant such as titanium dioxide, either to the synthetic linear polyamide prior to the formation of the fiber or to the surface of the finished fiber. Prior to the advent of this invention, it was generally impossible to achieve a suitable level of light durability simultaneously with a high delustering effect in synthetic linear polyamide yarns.

In general, the delustering agents useful in synthetic linear polyamide yarns are preferably finely divided materials such as pigments,

which have a refractive index differing from that of the polymer, which are incompatible therewith and which are inert thereto. The term "incompatible" is used with reference to such agents to indicate that the finely divided material is insoluble in the polymer at ordinary temperatures and forms a separate phase therefrom. For proper delustering, the added agent must be in a finely divided state and be so distributed throughout the polymer surface or fiber surface in order not to impair the continuity of the polymer or destroy its fiber quality.

The useful delusterants have an index of refraction which is different, i.e., lower or higher, from that of the polymer. The refractive index of the synthetic linear polyamides is approximately 1.55. The difference in refractive index between the delusterant and the polymer should be at least 0.05 and preferably more than 0.2. The most useful delusterants are those showing the greatest difference from the polymer. Titanium dioxide is particularly adapted for this use because of its high refractive index of 2.5 to 2.9, in compatibility with synthetic linear polyamides, low cost and availability.

It is an object of this invention to provide a light-durable delustered yarn of synthetic linear polyamide which has been delustered with a titanium dioxide pigment. Other objects of the invention will become apparent from the following description and claims.

It has now been found that shaped synthetic linear polyamides structures delustered with a pigment comprising an active oxide (hydrated oxide and/or oxide) of cerium chemically deposited without subsequent calcination on finely divided titanium oxide, have remarkably improved resistance to light degradation as compared with synthetic linear polyamide structures such as yarns delustered with ordinary titanium dioxide delusterants.

In the drawing, which is a graph showing the unexpected improvement in light-durability of the delustered polyamide yarns of this inven-

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tion in comparison with polyamide yarns delustered with the titanium dioxide pigments of the prior art.

Curve 1 shows the percent of the original tenacity of 70 denier nylon yarn, delustered with 2% of conventional anatase titanium dioxide, which remains after Weather-Ometer exposures of different durations,

Curve 2 is a similar showing for otherwise identical yarn delustered with a modified titanium dioxide pigment prepared by mixing finely divided titanium dioxide and hydrated cerium oxides.

Curve 3 is a similar showing for otherwise identical yarn delustered with a pigment prepared by precipitating titanium and aluminum oxides on finely divided titanium dioxide as described in Example 5,

Curve 4 is a similar showing for otherwise identical yarn delustered with a pigment prepared by treating finely divided titanium dioxide with cerous acetate as described in Example 6, and

Curve 5 is a similar showing for otherwise identical yarn delustered with a pigment prepared by precipitating hydrated cerium oxides on finely divided titanium dioxide as described in Example 1.

This pigment modification may be achieved as follows: Any of the ordinary titanium dioxide pigments of the trade, normally useful for yarn delustering purposes, is suspended in an aqueous medium which is acidified to a pH value of about 3. A soluble cerium salt is then added and an active form of cerium ion is precipitated as a mixed hydroxide or hydrated oxide or basic salt on the dispersed particles of titanium dioxide. After filtering and drying, the resulting pigment can be used as such or, if desired, the modified pigment can be comminuted before used. If desired, any cerium compound in the form of a hydroxide or basic salt on the titanium dioxide particles may be converted to the oxide by a suitable heat treatment, provided that the temperatures are kept well below the usual calcining temperatures; following this heating, comminution may be necessary. Still another method for producing these modified delusterants is by impregnating the calcined and ground titanium dioxide with a nitrate or similar salt of cerium, followed by a moderate heat treatment to convert said salt into the insoluble oxide. Any of these treatments may be accomplished with an appropriate salt or a mixture of compounds of cerium.

The calcined comminuted titanium dioxide useful in the invention may consist of titanium dioxide in any of its crystalline forms such as rutile or anatase. This material may likewise consist of any of the many titanium dioxide compositions resulting from the coprecipitation of various metal hydroxides with titanium hydroxide followed by the usual drying, calcining and grinding operations.

The invention will be more readily understood from the following examples which show the surprising improvement in light-durability of polyamide yarns delustered in accordance with this invention as compared with yarns delustered with prior art titanium dioxide pigments. Methods for preparing the delusterants of this invention detailed below are, of course, merely illustrative and not limitative.

EXAMPLE 1

Twenty parts by weight of finely ground titanium dioxide were suspended in 100 parts by weight of a solution containing 0.66 parts ceric bisulfate which is equivalent to 0.22 parts cerium oxides calculated as CeO_2 . The mixture was agitated continuously for 60 minutes, after which the pH of the solution was raised slowly to 8 by the addition of ammonium or sodium hydroxide. At pH 8, cerium oxides were precipitated on the TiO_2 particles in suspension. Some 50% of the water of the mixture was removed by filtration, and the filter cake was twice reslurried in fresh water in order to wash away water-soluble salts. The washed pigment was dried at 100°C . and ground.

EXAMPLE 2

Twenty parts by weight of finely ground titanium dioxide were suspended in 100 parts by weight of a solution containing 0.75 parts cerous nitrate which is equivalent to 0.3 parts ceria. The temperature was raised to 60°C . under continuous agitation and the agitation continued for 60 minutes at 60°C . The water was filtered off and the wet cake put into an oven at 200°C . for 18 hours to convert the cerous nitrate to the oxides of cerium. When analyzed, the pigment was found to have a cerium content of 1% by weight calculated as CeO_2 . The 50% excess originally present had been lost in the filtrate apparently. The heat-treated pigment was next ground to a suitable fine state for use as a delustering agent.

EXAMPLE 3

A portion of the washed pigment from Example 1 was calcined in the usual manner at red heat (800 – $1,000^\circ \text{C}$.), cooled, and ground. As shown in Example 9 this pigment was not better than conventional anatase titanium dioxide.

EXAMPLE 4

The pH of 100 parts by weight of a solution containing 2.1 parts ceric bisulfate (equivalent to 0.7 parts cerium oxides calculated as CeO_2) was slowly raised by adding sodium hydroxide solution while agitating vigorously. At pH 8, cerium oxides were precipitated. Most of the water was then removed by filtration and the filter cake was twice reslurried in fresh water to wash away the water-soluble salts. The cerium oxides were next slurried in with 20 parts of finely ground calcined titanium dioxide under vigorous agitation, the mixed

pigment filtered, and dried at 100° C. As shown in Example 10 this method of preparing a cerium-modified titanium dioxide pigment is not effective.

EXAMPLE 5

A titanium dioxide pigment possessing the crystal form of anatase and prepared by a sulfate process was held in the form of a finely divided aqueous suspension. The pigment suspension was treated with solutions containing 3 parts of dissolved TiO_2 and 2 parts of dissolved Al_2O_3 for each 100 parts by weight of pigment in the suspension. The titanium solution used was prepared by the solution of a titanium hydrolyzate in sulfuric acid, while the aluminum was dissolved by means of alkali and was in the form of sodium aluminate. The titanium solution was first added, followed by the sodium aluminate and the pH of the suspension was then adjusted to the neutral point with ammonium hydroxide. The resulting pigment was filtered, washed and dried. For the purposes of this invention, as shown by Example 11, this treatment with titanium salt is in no way equivalent to treatment with a cerium salt.

EXAMPLE 6

To 100 parts of a slurry containing 20 parts of ground anatase TiO_2 and 0.02 parts of sodium pyrophosphate as the dispersing agent were added 0.8 parts of cerous acetate hydrate. The cerous acetate was the calculated equivalent of 0.4 parts of CeO_2 . This slurry was used in the preparation of delustered polyhexamethylene adipamide according to the procedure indicated below. The slurry could be filtered and the paste obtained therefrom also employed in this delustering step. This indicated that an appreciable portion of the water-soluble cerous acetate had been absorbed on the titanium dioxide and was not removed in the filtering step. Apparently the cerous acetate under the rigorous conditions of polymerizing the polyamide is dissociated into the oxides of cerium and into acid which is picked up by the polyamide. The beneficial effect of the cerium added in this way was considerably less pronounced than in Example 1 as shown in Examples 8 and 12. The addition of cerous acetate solution alone to an already delustered polyamide-forming composition was without beneficial effect.

EXAMPLE 7

To 100 parts of a slurry containing 20 parts of finely ground anatase TiO_2 and 0.02 parts of sodium pyrophosphate as a dispersing agent were added 0.4 parts of cerous acetate hydrate. This slurry was used to deluster polyhexamethylene adipamide as described in Example 13. This example again serves to demonstrate that this method of adding cerium to the TiO_2 is not as efficient as the previously described methods. Here the cerium was equivalent to 0.2 parts calculated as CeO_2 .

In the preparation of the delustered filaments of this invention from polyamides, it is usual to deluster according to the process described in British Patent Specification No. 554,718, the polyamide being prepared as described in British Patent Specification No. 506,125. The resulting polyamide is converted to flake form as described in British Patent Specification No. 533,306. The nylon, polyhexamethylene adipamide, has been chosen to represent the polyamides since this material is currently of greatest importance commercially. Filaments and yarns of this representative polyamide, delustered with pigments prepared as described above, were prepared by melt spinning with an apparatus of the Greenwalt type as disclosed in U.S. Patent No. 2,217,743, and by drawing as described in British Patent Specification No. 543,466.

EXAMPLE 8

Two parts by weight of the pigment prepared in Example 1 were incorporated into 100 parts of polyhexamethylene adipamide and the delustered polymer converted into 70 denier, 34 filament yarn as described above. Analysis of this yarn for cerium content gave the value of 0.022% by weight calculated as CeO_2 . On testing in the Weather-Ometer, this yarn lost approximately 85% of its tenacity in 1,000 hours, compared to 130 hours for yarn delustered with an equivalent proportion of anatase TiO_2 (Curves 5 and 1 of the drawing). Similarly, in outdoor exposure the yarn containing this cerium-modified titanium dioxide lasted more than 22 weeks, compared with 14 weeks for the equivalent yarn containing anatase titanium dioxide. The pigment of Example 2 produces a like result.

EXAMPLE 9

A nylon yarn identical with that of Example 8, except that the delusterant was 2% anatase titanium dioxide, was prepared under the same conditions. When tested in the Weather-Ometer, this yarn lost 100% of its original tenacity in 190 hours (Curve 1 of the drawing). When tested outdoors, it lost 100% of its tenacity in 14 weeks. No different results were obtained when 2.3% of the calcined pigment of Example 3 was used instead of the anatase titanium dioxide pigment.

EXAMPLE 10

A nylon yarn identical with that of Example 8, incorporated the delusterant of Example 4. This yarn on testing in the Weather-Ometer lost 100% of its tenacity in 250 hours (Curve 2 of the drawing), hence showed scarcely any improvement over the control yarn delustered with anatase titanium dioxide.

EXAMPLE 11

A nylon yarn identical with that of Example 8, incorporated the delusterant of Example 5.

This yarn on testing in the Weather-Ometer lost 100% of its tenacity in 290 hours (Curve 3 of the drawing), hence was but little better than the control yarn.

5 EXAMPLE 12

A nylon yarn identical with that of Example 8, incorporated the delusterant of Example 6. This yarn on testing in a Weather-Ometer lost 100% of its tenacity in 1000 hours (Curve 10 4 of the drawing).

EXAMPLE 13

A nylon yarn identical with that of Example 8, incorporated the delusterant of Example 7. This yarn on testing in a Weather-Ometer lost 15 100% of its tenacity in 400 hours.

In the light-durability test a single layer of the yarn was wound on a panel of non-metallic material, the single filaments being well separated for convenience in removal. The panel was exposed to radiation in a standard Weather-Ometer. In this well-known instrument, samples were mounted on a drum revolving at 1 revolution per minute and placed 15 inches from a mercury arc lamp surrounded by a 25 Pyrex envelope. The enclosure was heated and humidified so as to maintain a panel temperature of approximately 110° F. and approximately 90% relative humidity. The test was distinguished from an indoor weathering 30 test in that the yarn on the panel was not sprayed. Every 20 to 25 hours the test was interrupted to change carbon arcs and wash the glass envelope. Every 50 or 100 hours, the panel was taken out of the device and five 35 strands of yarn removed for a determination of break strength and of elongation at the break point. These determinations were then compared with those determined on the unexposed yarn.

In outdoor exposures the same type of panels were used to support the yarn, but the sampling interval was increased to two weeks. In all exposure tests, controls were included to prevent the significance of results from being obscured by changing conditions, particularly the seasonal changes outdoors. The test results given herein were run in Wilmington, Delaware during the winter months.

It is apparent from the foregoing specification that the mere combination of cerium oxides and titanium oxides does not result in a pigment which, when incorporated into a highly delustered nylon yarn, gives unusual 55 light durability. It appears to be essential in order to obtain marked improvement in light-durability to form the cerium hydroxides (hydrated oxides) and/or oxides directly on the surface of previously prepared titanium dioxide particles. Furthermore, the action of cerium oxides is unique in the beneficial effect on light durability since neither titanium hydroxides or oxides nor aluminum hydroxides

or oxides when similarly applied produce the startlingly beneficial effect. 65

It is further demonstrated that cerium-containing calcined pigments of the prior art (Examples 3 and 9) did not produce the beneficial effect produced by the pigments of this invention, even though a chemical analysis might have led one to believe that the two types of pigments were identical. Any calcining treatment after precipitating the cerium hydroxides and/or oxides on the surface of the titanium dioxide particles inactivates the cerium, destroying the capacity of the pigment to give improved light durability to highly delustered nylon yarn. It has also been shown that the mere mixing of the already formed hydroxides and/or oxides of cerium with calcined titanium dioxide particles does not give a pigment which produces the beneficial results of the pigment of this invention (Examples 4 and 10). The cerium oxide modifier must be chemically deposited in active 75 form. 80

The titanium dioxide pigments of this invention may have a cerium content calculated as cerium dioxide ranging from 0.5% up to 5% or even more. However, it is preferred that the cerium content fall within the range of 0.5 to 2.0% in order to give nylon yarns of optimum properties. Only modest improvement in light durability is achieved by increasing the cerium content of the titanium dioxide much above 2%. At the same time in these higher ranges much above 2%, yarn abrasiveness is undesirably increased. The amount of modified pigment used for delustering may range from 0.1% to 10.0% or even more of the weight of the polyamide, with 0.1% to 5.0% ordinarily being employed. 90 95 100

The improvement in light-durability characteristics of the highly delustered yarns of this invention is not obtained with similarly delustered yarns of all synthetic linear condensation polymers. For example, when a highly delustered yarn of polyethylene terephthalate was prepared as described in British Patent Specification No. 578,079 it was found that anatase titanium dioxide gave as good results as the pigment of this invention. In these 70 denier, 34 filament yarns, each containing 2% delusterant, both lost 25% of their tenacity in 1,000 hours exposure in a Weather-Ometer. The pigment of this invention is believed, therefore, to be particularly effective with respect to polyamides. 110 115

What we claim is:—

1. A shaped synthetic linear polyamide structure delustered with a pigment comprising an active oxide (hydrated oxide and/or oxide) of cerium deposited without subsequent calcination on finely divided titanium oxide. 120

2. A shaped synthetic linear polyamide structure delustered with a pigment comprising finely divided particles of titanium dioxide having from 0.5% to 5%, preferably 0.5% to 125

- 2% of active cerium oxide, calculated as cerium dioxide, deposited directly on the surface of the particles without subsequent calcination.
- 5 3. A shaped synthetic linear polyamide structure having dispersed therein from 0.1% to 10.0% of a pigment comprising finely divided particles of titanium dioxide modified with an active oxide of cerium deposited on the surface of the particles without subsequent calcination.
- 10 4. A synthetic linear polyamide yarn delustered with from 0.1% to 5.0% of a pigment comprising finely divided particles of titanium dioxide having from 0.5% to 2.0% of active cerium oxide, calculated as cerium dioxide, deposited directly on the surface of the particles without subsequent calcination. 15

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767,897 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

LIGHT DURABILITY OF 70 DENIER NYLON YARNS
DELUSTERED WITH 2% OF VARIOUS TITANIUM DIOXIDE PIGMENTS

